

The Effects of CO, C₂H₄, and H₂O on the NO_x Storage Performance of Low Temperature NO_x Adsorbers for Diesel Applications

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ABSTRACT

Model low temperature NO_x adsorbers (LTNA) consisting of Pd on a ceria/zirconia washcoat on monoliths were evaluated for low temperature NO_x storage under lean conditions to assess their potential for adsorbing the cold-start NO_x emissions on a diesel engine during the period before the urea/SCR system becomes operational. A reactor-based transient test was performed with and without C₂H₄, CO/H₂, and H₂O to assess the effects of these species on the NO_x storage performance. In the absence of C₂H₄ or CO/H₂, H₂O severely suppressed the NO_x storage of these model LTNAs at temperatures below 100°C, presumably by blocking the storage sites. When C₂H₄ was included in the feedgas, H₂O still suppressed the NO_x storage below 100°C. However, the C₂H₄ significantly increased the NO_x storage efficiency above 100°C, attributable to the formation of alkyl nitrites or alkyl nitrates on the catalyst. When the feedgas contained CO/H₂, the NO_x storage performance was greatly improved below 100°C, even in the presence of H₂O. Tests with CO alone and H₂ alone indicated that CO was providing the improved NO_x storage capability. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analysis on a Pd/ceria powder indicated that NO and CO react to form NCO at low temperatures, which could account for the improved NO_x storage in the presence of CO. The formation of alkyl nitrites or nitrates with NO and C₂H₄ could not be confirmed or denied because the spectra for these species occur in the same range as that of carbonates which form from the C₂H₄.

CITATION: Theis, J. and Lambert, C., "The Effects of CO, C₂H₄, and H₂O on the NO_x Storage Performance of Low Temperature NO_x Adsorbers for Diesel Applications," *SAE Int. J. Engines* 10(4):2017, doi:10.4271/2017-01-0942.

INTRODUCTION

Selective Catalytic Reduction (SCR) of NO_x with NH₃ is highly effective for reducing the NO_x emissions from diesel engines once the SCR catalyst reaches a temperature of ca. 200°C [1]. Due to the hazards of storing gaseous NH₃ on vehicles, automakers currently inject an aqueous solution of urea [CO(NH₂)₂] from a storage tank into the exhaust upstream of the SCR catalyst, and each urea molecule thermally decomposes into two molecules of NH₃. However, because of the low exhaust temperatures and therefore the slow warm-up of the exhaust system on diesel engines, up to 200 seconds can be required for the SCR catalyst to reach 200°C. The urea injection and therefore the NO_x reduction must be delayed during this warm-up period, resulting in significant NO_x slip from the vehicle.

To satisfy stringent emission regulations such as the California SULEV30 standard or the Federal Tier 3 standard, it would be desirable for a low temperature NO_x adsorber (LTNA) to adsorb the NO_x during the initial cold start period and then release the NO_x once the SCR catalyst reaches 200°C and the urea injection system is activated. To facilitate the release of the NO_x from the LTNA after the vehicle is warmed up, it would be desirable for the LTNA to store the NO from the engine as nitrites rather than oxidizing the NO to NO₂ and forming nitrates, as nitrites are thermally less stable than nitrates and therefore easier to decompose [2]. LTNAs often utilize materials such as ceria and

alumina to store NO_x and avoid barium or other alkaline-earth metals, as these materials can form stable nitrates which are difficult to decompose under lean conditions.

In one of the early investigations into passive NO_x adsorbers, Millo and Vezza assessed a diesel oxidation catalyst (DOC) with NO_x storage capability [3]. While the NO_x capacity decreased after hydrothermal aging at 750°C, there was still sufficient capacity to decrease the overall NO_x emissions from the vehicle during NEDC tests.

Coulson et al. [4] and Melville et al. [5] reported that palladium (Pd) on ceria can store NO directly without forming NO₂. Chen [6] presented a diesel Cold Start Catalyst dCSC™ that incorporated the Pd/ceria component of Coulson and Melville along with a hydrocarbon trapping component. Chen [7] also discussed a NO_x adsorber that eliminated the Pd/ceria component and utilized Pd supported on multiple types of zeolite in order to expand the temperature range in which NO could be stored and to improve the sulfur tolerance of the catalyst.

Crocker et. al. [8] investigated powders of 1% Pt on Al₂O₃ and 1% Pt on Al₂O₃ stabilized with 1 to 10% lanthanum (La) for NO_x storage and release. It was found that 1% La improved the storage efficiency of NO_x but hindered the release of the NO_x. H₂O and CO₂ hindered the NO storage performance but improved the desorption efficiency.

Theis and Lambert [9] investigated several monolithic LTNAs on a reactor-based transient test that partially simulated the thermal environment of the DOC during the first two phases of the Federal Test Procedure (FTP-75) following by a supplemental FTP (US06) test on the Ford Super Duty diesel truck. A Pt-only LTNA and a Pt-rich bimetallic (Pt/Pd) LTNA had low NO_x storage performance during the first 200 seconds of the test due to low NO adsorption efficiency and low NO oxidation capability at low temperatures. However, a Pd-rich bimetallic (Pt/Pd) LTNA had good NO and C₂H₄ storage efficiency during the first 200 seconds of the test. Most of the NO_x release from the Pd-rich LTNA was in the form of NO, but the Pt-only and Pt-rich formations generated high levels of NO₂.

Theis [10] assessed several model LTNAs consisting of 0.92 grams per liter (g/L) of either Pt or Pd on washcoats of either alumina or ceria/zirconia (CZO) supported on monoliths in order to assess the contributions of the washcoat and the precious metal on the NO_x storage performance. The LTNAs were evaluated on the reactor-based transient test after lean treatments at 700°C and after rich treatments at 350°C to assess the effects of the pretreatment on the storage and release performance. After oxidation, Pd on CZO was found to provide the best combination of good NO_x storage efficiency in the presence of H₂O and C₂H₄, good purgability as the result of storing NO directly, low generation of NO₂ and N₂O, and cost effectiveness relative to its Pt counterpart. The oxidized Pd on Al₂O₃ provided very low NO_x storage capability, suggesting that ceria is an important contributor to the NO_x storage performance.

In this study, a model LTNA with a low loading of Pd on a CZO washcoat and a model LTNA with a higher loading of Pd on a CZO washcoat were evaluated for NO_x storage and release performance on the reactor-based transient test. Using C₂H₄ as a representative hydrocarbon, the tests were performed with and without H₂O, C₂H₄, and CO/H₂ in order to evaluate the effects of these exhaust species on the NO_x storage performance. The effects of the NO concentration, the space velocity, and the NO_x species (i.e., NO vs NO₂) were also assessed. To investigate the surface species that form during the NO_x storage process, DRIFTS analysis was performed on a powder sample of ceria impregnated with Pd during exposure to a lean environment with NO alone, CO alone, and a mixture of NO and CO.

EXPERIMENTAL

Catalysts

The monolithic core samples used in the reactor testing were degreased model LTNAs with a diameter of 2.54 cm. The low loaded sample was 10.2 cm in length, had a cell density of 400 cells per square inch (CPSI), a wall thickness of 4 mils, and was loaded with 0.92 g/L (26 gpcf) Pd on a 50/50 mixture of ceria and zirconia (CZO), where the washcoat loading was approximately 61 g/L. The high loaded sample had a cell density of 900 CPSI, a wall thickness of 2 mils, contained 2.76 g/L (78 gpcf) Pd on a mixture of ceria and zirconia, and the washcoat loading was approximately 183 g/L. The high loaded sample was evaluated with lengths of 2.54, 5.08, 7.62, and 10.2 cm to assess the effects of the gas hourly space velocity on the NO_x storage performance. Prior to testing, the samples were degreased on the reactor with 10% O₂, 5% H₂O, 5% CO₂, and the

balance N₂ at temperatures of approximately 700°C. Small holes were drilled into the axial centers of the rear faces of the monoliths to a depth of 5 to 10 mm so that a type K thermocouple could be inserted into the rear face of the catalyst for measuring the bed temperature during the tests.

Experimental Apparatus

The laboratory reactor used for the transient testing is illustrated in Figure 1. A transient test was performed on the reactor to expose the catalyst sample to a subset of the DOC temperatures on the Ford Super Duty diesel truck during the first two phases of the FTP-75 test following by a supplemental FTP (US06) test. The test was performed by cooling the oven to 70°C and placing the reactor in bypass mode. 70°C was chosen as the starting temperature rather than room temperature to allow more tests to be performed during a day. The oven thermocouple located outside of the quartz tube was used for feedback to the oven controller. For most tests, the feedgas contained 100 to 130 ppm NO, 5% CO₂, 10% O₂, and N₂ as the balance. To assess the influence of H₂O, CO/H₂, and C₂H₄ on the NO_x storage performance, tests were performed with and without 5% H₂O, with and without 1350 ppm CO and 450 ppm H₂, and with and without C₂H₄ (either 250 or 500 ppm). C₂H₄ was used as a representative hydrocarbon because it is often present in high concentrations in diesel exhaust. For most of the tests, CO and H₂ were supplied from a single bottle and were in a 3:1 ratio. However, CO alone (i.e., without H₂) was used on a small number of tests.

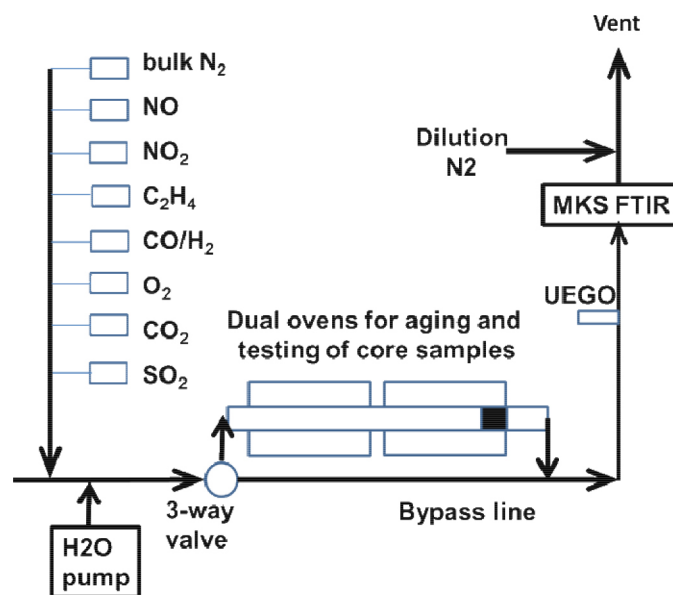


Figure 1. Experimental apparatus for aging and testing of core samples.

Once the gas concentrations and bed temperature were stabilized, the exhaust was directed through the sample, and the oven was immediately ramped from 70°C to 175°C at 10°C/min and then held at 175°C for 10 minutes to simulate the first two phases of the FTP-75 test. The oven was then ramped from 175°C to 300°C at 10°C/min and held for 5 minutes to simulate the US06 test. The flow rate was held constant at 6.4 L/min during the test, resulting in a space velocity of 30,000 h⁻¹ for a 2.54 cm long core sample and 7,500 h⁻¹ for a 10.2 cm long core sample.

The test was originally used with 2.54 cm long samples, and for this sample length the maximum and stabilized bed temperatures during the FTP-75 simulation were 250°C and 200°C, while the maximum temperature during the US06 simulation was ca. 350°C. These temperatures agreed well with the measured exhaust temperatures before and after the DOC on the Super Duty truck during the FTP-75 and US06 tests. However, with the 10.2 cm long samples, the corresponding bed temperatures were slightly higher at 280°C, 230°C, and 400°C, respectively.

While the total test required 38 minutes to perform, emphasis was placed on the average NO_x storage efficiency during the period that the bed temperature of the catalyst was below 200°C, since this is the period when urea is not flowing on the vehicle. The time to achieve 200°C in the DOC varies with the application and the heating strategy. On the Ford Super Duty truck, this time is approximately 200 seconds. The reactor used in this project heated up more slowly than the vehicle, and the time to achieve 200°C was approximately 310 to 320 seconds. The NO_x storage efficiency was averaged over this time period using equation (1):

$$\text{Ave NO}_x \text{ Storage Efficiency} = 100\% * \{ 1 - \int \text{exitNO}_x dt / t @ T=200^\circ\text{C} / \text{FGNO} \} \quad (1)$$

where the integral is performed while the bed temperature is under 200°C, FGNO refers to the feedgas concentration of NO, and exitNO_x refers to the NO_x concentration (i.e., NO+NO₂) in the exhaust exiting the reactor, measured with a 1 Hz MKS Fourier transform infrared (FTIR) analyzer equipped with an inlet sample line heated to 191°C.

DRIFTS Analysis

To investigate the surface species that develop during NO_x storage in the presence of CO, a powder catalyst was prepared consisting of 2% Pd on pure ceria. This powder was placed into the sample holder of a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analyzer (Nicolet 6700 FTIR spectrometer with a praying mantis cell) at Ford. After heating to 100°C, the sample was exposed to 300 ppm NO, 10% O₂, and the balance N₂ for 120 min. Spectra were collected periodically during the 120 min storage period. The NO was turned off, and the sample was heated in steps of 50°C to 650°C. Spectra were collected during the steady-state periods while the temperature was increasing (i.e., with stored NO_x) and while the temperature was decreasing (i.e., without the stored NO_x). A similar procedure was performed with 850 ppm CO, 10% O₂, and the balance N₂. Finally, the same procedure was performed with 300 ppm NO, 850 ppm CO, 10% O₂, and the balance N₂.

DRIFTS work was also performed at the Center for Applied Energy Research (CAER) at the University of Kentucky in support of this project [11]. A Nicolet 6700 IR spectrometer equipped with a Harrick Praying Mantis accessory and MCT (mercury-cadmiumtelluride) detector was used for this work. Approximately 50 mg of 2% Pd on ceria was loaded into the reaction cell, pretreated in 5% O₂ in argon (Ar) at 500°C for 60 min, cooled to 100°C in 5% O₂ in Ar, and then

purged with Ar. The catalyst was then exposed to 300 ppm NO, 750 ppm C₂H₄, and 5% O₂ in Ar at 100°C for 20 min, and spectra were recorded periodically during the 20 min period.

RESULTS AND DISCUSSION

Effect of H₂O, C₂H₄, and CO/H₂ on NO_x Storage

The degreased 10.2 cm long Pd/CZO catalyst with 0.92 g/L Pd was evaluated on the transient test with and without 250 ppm C₂H₄ and with and without 5% H₂O. Figure 2 displays the results of one test each with the four combinations of gases during the first 800 seconds of the tests. The dashed vertical line at 319 seconds indicates when the bed temperature of the sample achieved 200°C. In the absence of H₂O and C₂H₄, the catalyst was fairly effective for storing NO_x during the initial portion of the test, and the NO_x slip did not approach the feedgas level until ca. 500 seconds. There was a small release of NO_x beginning at 540 seconds, where the NO_x slip exceeded the feedgas level for a period of time. During the test with C₂H₄ but no H₂O, the NO_x slip followed approximately the same trajectory as the slip on the test without C₂H₄ or H₂O for the first 80 seconds. However, at that point the NO_x dropped dramatically and achieved a maximum storage efficiency of 80% at 190 seconds. While not shown, the C₂H₄ slip dropped at the same time that the NO_x slip dropped. There was also more NO_x released between 500 and 700 seconds on the test with C₂H₄, indicating that more NO_x was stored in the presence of C₂H₄.

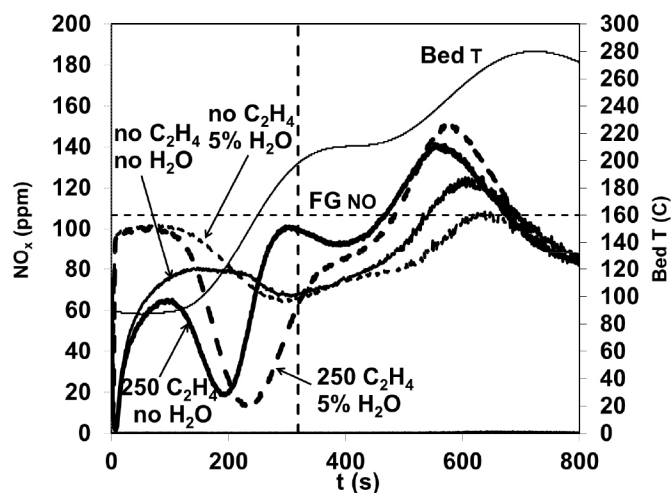


Figure 2. NO_x emissions for 10.2 cm long Pd/CZO catalyst with 0.92 g/L Pd during one transient test each with and without 250 ppm C₂H₄, with and without 5% H₂O, 110 ppm NO, 5% CO₂, and 10% O₂.

On the tests with H₂O (with and without C₂H₄), the NO_x storage was severely suppressed while the bed temperature was below 100°C. This was attributed to the water condensing and blocking the NO_x storage sites. On the reactor, a significant amount of time was required for the bed temperature to start increasing due to the thermal inertia of the oven and the sample. As a result, the time that the bed temperature was below 100°C was on the order of 150 seconds. This long induction period on the reactor amplified the deleterious effect of water on the NO_x storage performance. After the bed temperature exceeded 100°C, the NO_x slip dropped only modestly on the test without C₂H₄. There was also very little NO_x released between 500

and 700 seconds on that test, confirming that very little NO_x had been stored. However, similar to the test with C_2H_4 but no H_2O , the NO_x slip on the test with C_2H_4 and H_2O dropped dramatically after the bed temperature exceeded 100°C and reached a maximum NO_x storage efficiency of ca. 88% at 240 seconds. The NO_x release was also higher between 500 and 700 seconds on this test and was similar in magnitude to the NO_x release on the test with C_2H_4 but without H_2O , again confirming that more NO_x had been stored.

So C_2H_4 significantly increased the amount of NO_x stored and released on the catalyst, both in the presence and absence of H_2O . This improved NO_x storage performance was attributed to an interaction between NO and C_2H_4 that increased the amount of NO_x that was stored, possibly through the formation of alkyl nitrites or alkyl nitrates [8]. This potential mechanism will be discussed further during the analysis of the DRIFTS data.

While not shown here, most of the NO_x emissions from this Pd/CZO catalyst were in the form of NO , particularly during the FTP-75 simulation. Significant NO_2 did not appear until the end of the US06 simulation, when the bed temperatures were between 300 and 400°C . Since the NO_x release occurred under lean conditions and NO was the primary species observed even when there was no reductant (i.e., C_2H_4) present that could potentially reduce NO_2 to NO , this suggested that the catalyst was storing NO directly, possibly as nitrites, and NO was not oxidized to NO_2 to form nitrates. Since nitrites are easier to decompose than nitrates, this would be beneficial for purging the catalyst of stored NO_x during warmed-up operation so that it would be able to store the maximum amount of NO_x on the next cold start test.

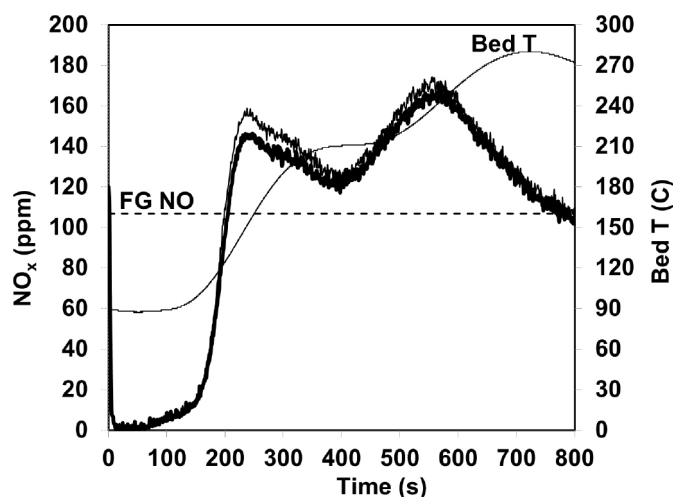


Figure 3. NO_x emissions during two transient tests on 10.2 cm long Pd/CZO catalyst with 0.92 g/L Pd. Tests performed with 110 ppm NO , 1200 ppm CO , 5% H_2O and CO_2 , and 10% O_2 .

The low loaded catalyst was also evaluated on two tests with 110 ppm NO , 1200 ppm CO (without H_2), 5% CO_2 and H_2O , and 10% O_2 , and the results are shown in Figure 3. Unlike the results with H_2O in Figure 2, where the H_2O severely suppressed the NO_x storage performance below 100°C with or without C_2H_4 , the NO_x storage efficiency below 100°C was nearly 100% for up to 60 seconds when

the feedgas contained CO , even in the presence of H_2O . While not shown here, tests with CO alone and H_2 alone indicated that CO was providing the improved NO_x storage capability. Similar to the proposed interaction between NO and C_2H_4 , there appears to be a beneficial interaction between NO and CO that significantly improved the NO_x storage performance at low temperatures, even when H_2O was present. This potential interaction between NO and CO will also be addressed during the DRIFTS analysis.

Effect of Pd Loading

To assess the effects of the Pd loading, tests were performed on the 10.2 cm long samples with 2.76 g/L Pd and 0.96 g/L Pd. Figure 4 compares the NO_x slip for two tests on the sample with 0.96 g/L Pd and for two tests on the sample with 2.76 g/L Pd when evaluated with 110 ppm NO , 250 ppm C_2H_4 , 5% CO_2 , and 10% O_2 but no H_2O . In the absence of H_2O , the higher-loaded sample had significantly better NO_x storage performance than the low-loaded sample and stored essentially 100% of the NO_x for over 4 minutes. The average NO_x storage efficiency of the high loaded sample while the bed temperature was below 200°C was approximately 98%, compared with 49% for the low-loaded sample. However, when the feedgas contained 5% H_2O , Figure 5 shows that the high loaded sample performed similarly to the low loaded sample for the first 200 seconds of the test. As mentioned earlier, the deleterious effect of H_2O was amplified on the reactor due to the extended time that the sample was below 100°C . The higher loaded sample did store more NO_x between 200 and 350 seconds. As a result, the average NO_x storage efficiency while the bed temperature was below 200°C was 58% for the higher loaded sample, compared with 40% for the lower loaded sample. The higher loaded sample also released significantly more NO_x than the lower loaded sample between 500 and 700 seconds, confirming that more NO_x had been stored. So the higher Pd loading significantly improved the NO_x storage performance of the LTNA, both in the absence of H_2O and at temperatures above 100°C in the presence of H_2O .

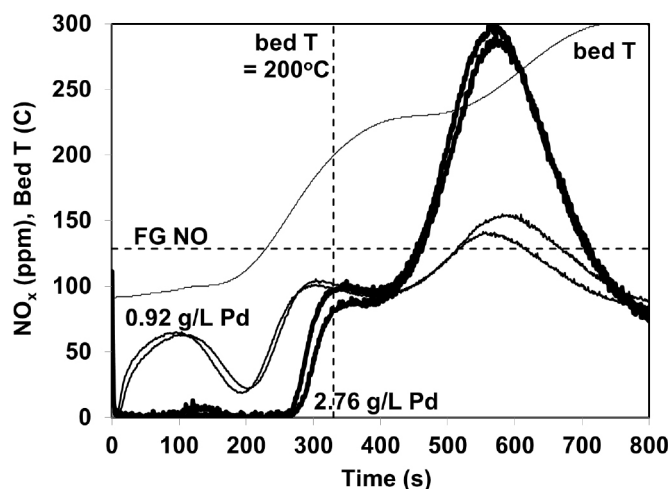


Figure 4. NO_x emissions during two transient tests each for 10.2 cm long Pd/CZO catalysts with 0.92 g/L Pd and 2.76 g/L Pd. Tests performed with 110 ppm NO , 250 ppm C_2H_4 , 5% CO_2 , 10% O_2 , but no H_2O .